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## 5.0 Analytical Methods

### 5.1 Field Analyses

Data for field analyses for the USCG monitoring wells and multi-level samplers are found in Appendices A and C. Monitoring well data for the DFC site are found in Appendix B.

#### 5.1.1 Hexavalent Chromium

At the USCG site, a 20- or 50-mL sample of unfiltered ground water was collected to determine Cr(VI) concentrations colorimetrically with a UV/VIS spectrophotometer (Hach® DR100 or Hach® DR/2010). Cr(VI) was analyzed directly using 1,5-diphenylcarbazide (Chroma-Ver3) as the complexing agent (American Public Health Association et al., 1992). This reagent contains a pH buffer combined with 1,5-diphenylcarbohydrazide, which results in a light purple color which is proportional to the amount of Cr(VI) present. Maximum detection limits for Cr(VI) using the Hach® DR/2010 spectrophotometer and the Hach® Pocket Colorimeter are 0.60 mg/L and 0.50 mg/L, respectively. Samples exceeding these maximum detection limits were diluted in the field prior to analysis. Minimum detection limits using these methods were 0.01 - 0.02 mg/L. Chromium was not a contaminant of concern at the DFC site and, therefore, was not analyzed.

There are very few interferences for this field test kit; however, iron and vanadium will interfere at concentrations >1 mg/L. Generally, the presence of ferrous iron in ground waters is indicative of reducing environments; therefore, Cr(VI) would not be expected in the ground water containing elevated concentrations of iron. Mercurous and mercuric irons may also cause slight interferences. Vanadium interference can be eliminated by waiting 10 minutes following the addition of the Chroma-Ver3 before analyzing the sample. Highly buffered ground water or extreme sample pH may exceed the buffering capacity of the reagents and sample pretreatment may be required.

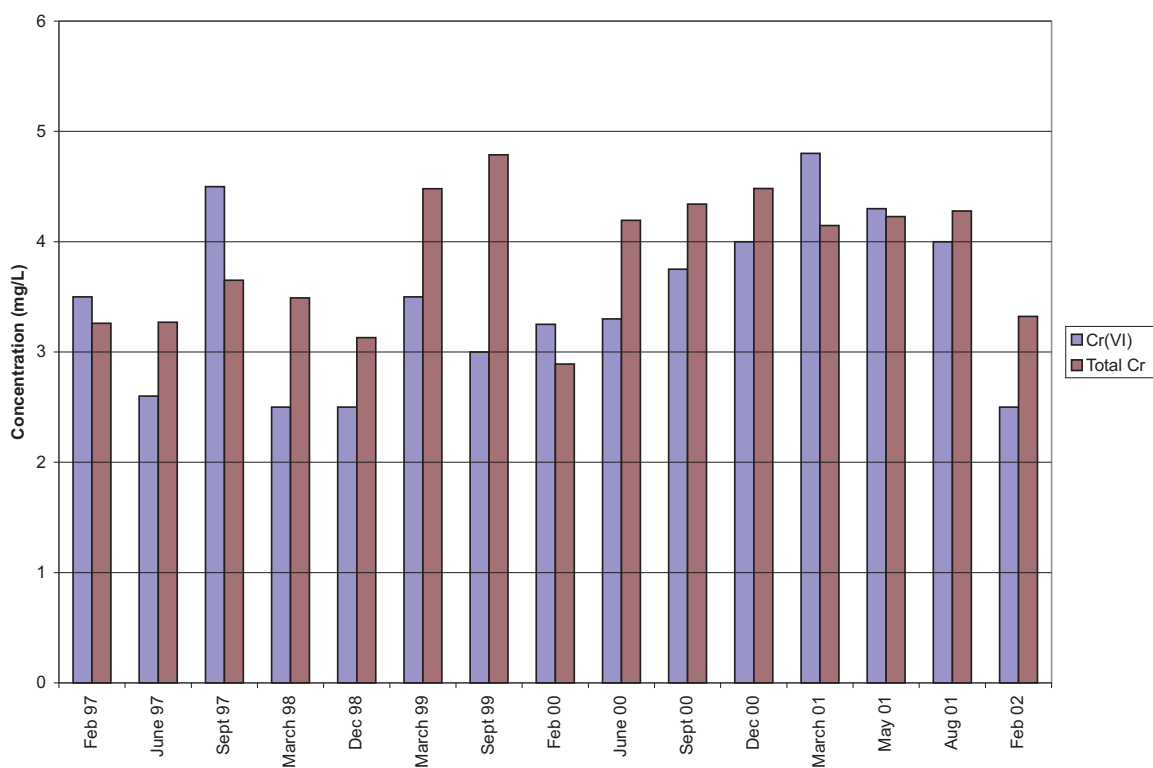
##### 5.1.1.2 Hexavalent chromium comparison with total chromium

At the Elizabeth City site the chromium plume is located upgradient of the PRB between 4.5 and 5.5 m below ground surface. Data show that most of the chromium is present as Cr(VI), which is highly mobile. The highest Cr(VI) concentrations were seen in MW13 just downgradient of the chromium source area. Total chromium and Cr(VI) values for monitoring wells and Transect 2 are shown in Tables A2, C9, C11, and C28, respectively. Figure 5.1 shows slight fluctuations in total chromium and Cr(VI) in MW13 with time; however, no seasonal trends are seen. A dramatic decrease in chromium concentration is seen in MW48 over time as treated water reaches this downgradient monitoring well (Figure 5.2). The regression analysis shown in Figure 5.3 for two monitoring wells MW13 and MW48 indicates an excellent correlation between total chromium and Cr(VI) values with an R<sup>2</sup> value of 0.93 and a slope of 1.06. Regression analysis was conducted for ML21 in Transect 2 and is shown in Figure 5.4. Where slightly higher values of total chromium are seen, colloidal particles could have passed through the 0.45 µm filter. Acidification of ground water may have released the colloidal chromium, resulting in the measured total chromium concentrations being higher than the actual aqueous Cr(VI) values measured in the field. Analytical variability, particularly for Cr(VI) where additional error is introduced by dilution of some samples during field analysis, may also be responsible for some of these concentration differences.

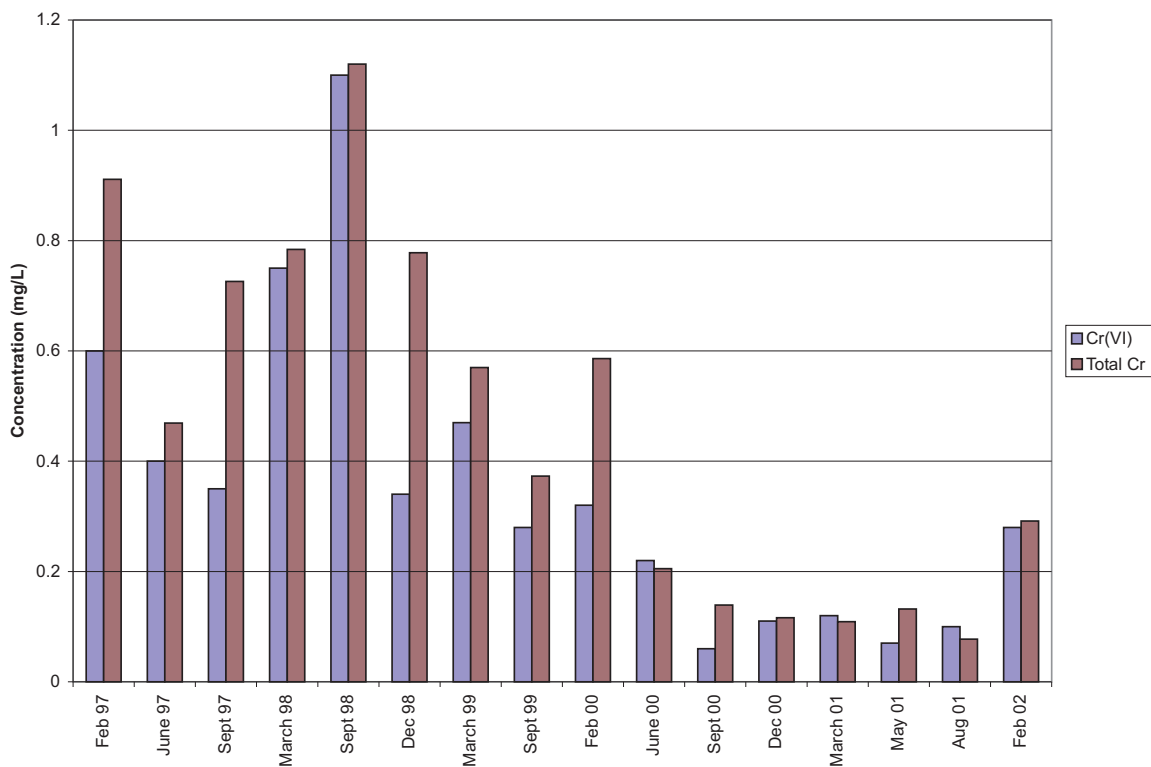
#### 5.1.2 Ferrous Iron

Ferrous iron (Fe<sup>2+</sup>) was measured in the field on unfiltered samples using two methods for comparison purposes. First Fe<sup>2+</sup> was measured using CHEMets® colorimetric test kits. Water was allowed to flow through a CHEMets® over-flow cell for at least three minutes and then sampled into CHEMets® ampoules containing 1,10 phenanthroline reagent (American Public Health Association et al., 1992). Following manufacturer's recommendations, the tip of the ampoule was placed at the bottom of the over-flow cell and then the tip was snapped off, allowing the ampoule to fill with ground water. The contents of the ampoule form an orange color in the presence of Fe<sup>2+</sup>. Following a 30 second equilibration period, the ampoule was visually compared with ampoules of known Fe<sup>2+</sup> concentrations.

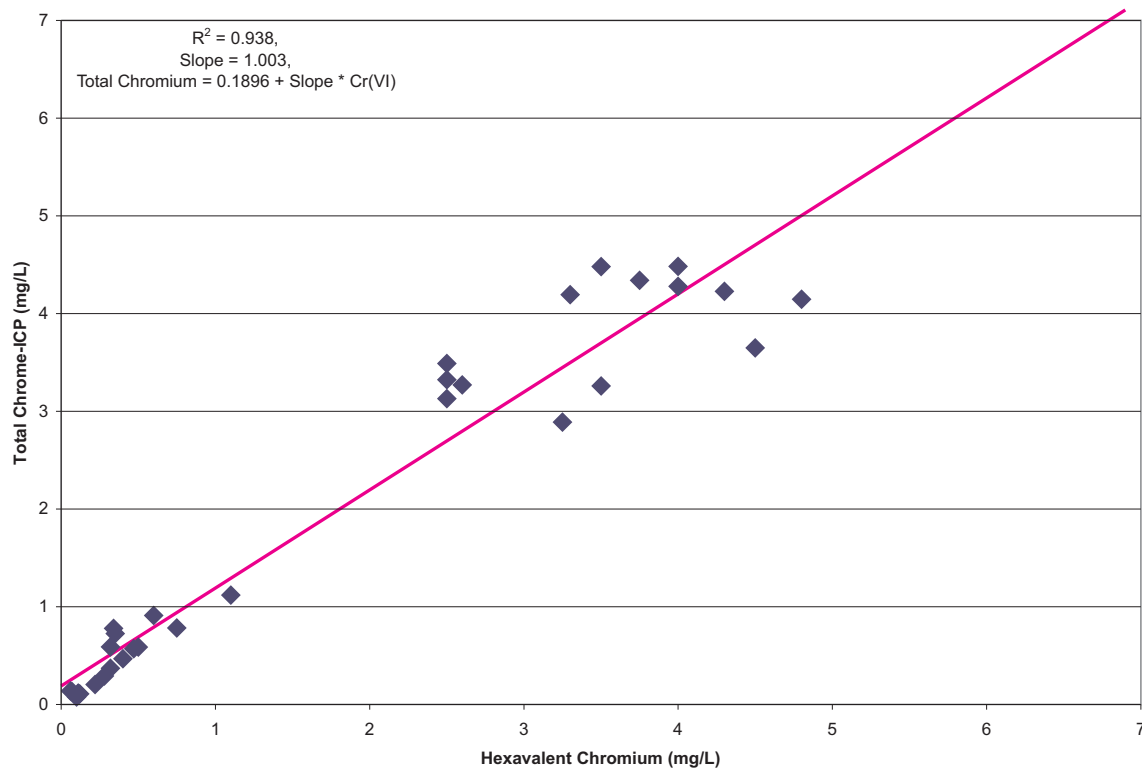
Fe<sup>2+</sup> was also determined using a Hach® DR/2010 spectrophotometer using 1,10 phenanthroline (FerroVer) as a complexing agent. Ferrous iron will oxidize rapidly to form ferric iron, especially at pH >8 which is typical in Fe<sup>0</sup> reactive zones. In order to minimize oxidation reactions, ferrous iron analysis was conducted immediately after sample collection.



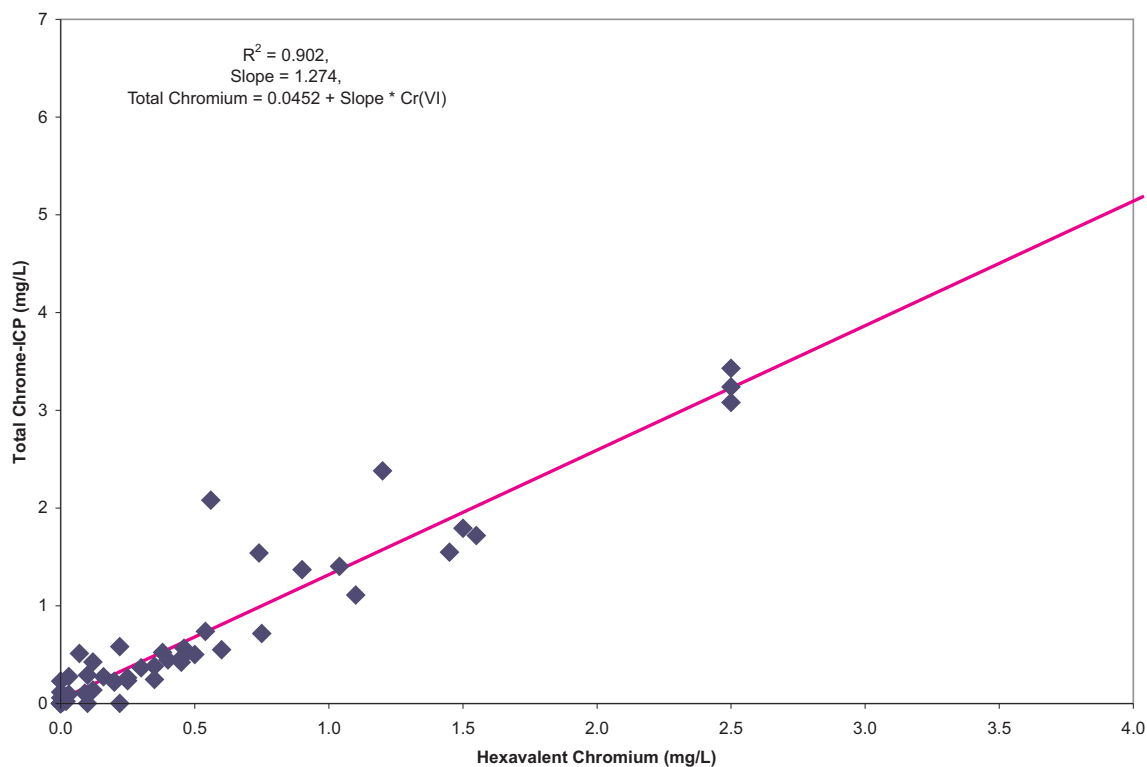
**Figure 5.1** Comparison of total chromium and Cr(VI) in monitoring well MW13 at the Elizabeth City site.



**Figure 5.2** Comparison of total chromium and Cr(VI) in monitoring well MW48 at the Elizabeth City site.



**Figure 5.3** Analysis of MW13 and MW48 comparing total chromium and Cr(VI) at the Elizabeth City site.



**Figure 5.4** Analysis of ML21 comparing total dissolved solids with specific conductance values at the Elizabeth City site.

It is important to add the FerroVer to the sample cell prior to adding the water sample in order to minimize oxidation of the  $\text{Fe}^{2+}$  prior to analysis.

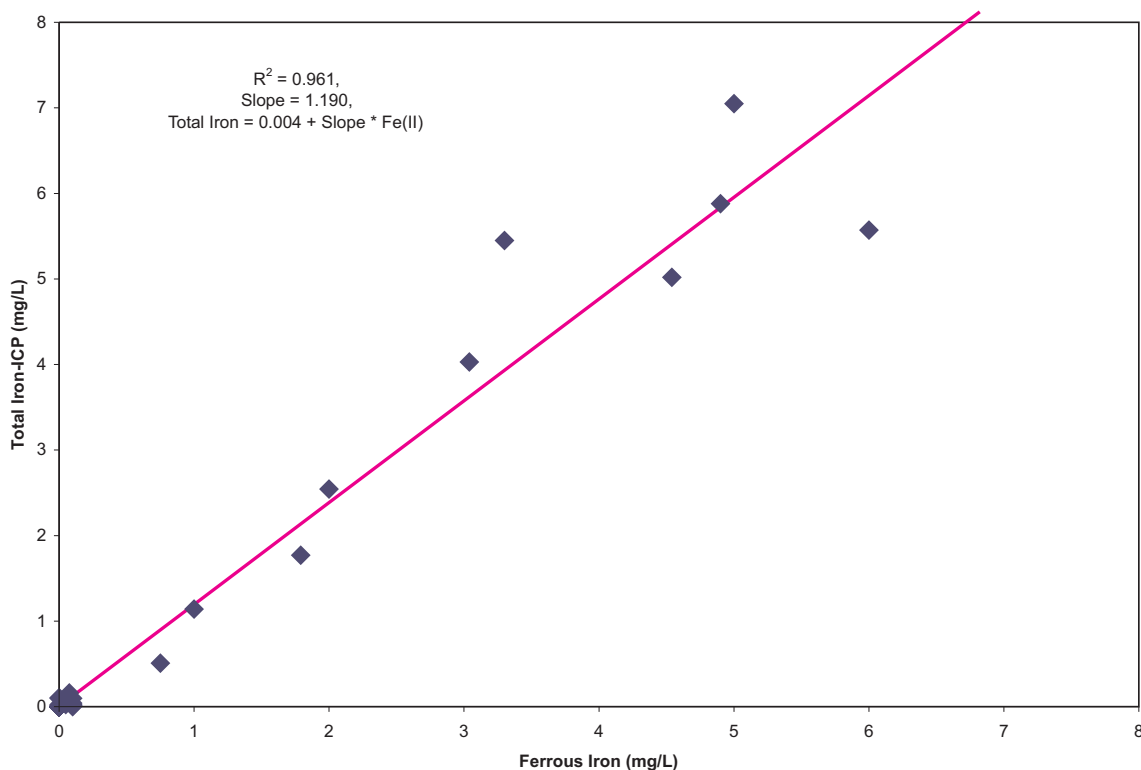
The maximum detection limit of the Hach® DR/2010 spectrophotometer is 3.00 mg/L. Where initial  $\text{Fe}^{2+}$  concentrations using the CHEMets® kit were determined to be  $>3.00$  mg/L, the sample was diluted prior to analysis using the Hach® DR/2010 spectrophotometer. It is important to consider potential interferences using these field test methods which can adversely impact  $\text{Fe}^{2+}$  measurements. Interferences include strong oxidizing agents, cyanide, nitrite, and phosphates. Polyphosphates have greater impact than orthophosphates. Certain metals may also interfere with  $\text{Fe}^{2+}$  measurements, including chromium, zinc, copper, nickel, and cobalt. However, chromium and zinc concentrations must be ten times greater than the ferrous iron present. Cobalt and copper must be greater than 5 mg/L and nickel in excess of 2 mg/L. Additionally, bismuth, cadmium, mercury, molybdate, and silver all precipitate the phenanthroline used in the analysis (American Public Health Association et al., 1992).

### 5.1.2.1 Ferrous iron comparison with total iron

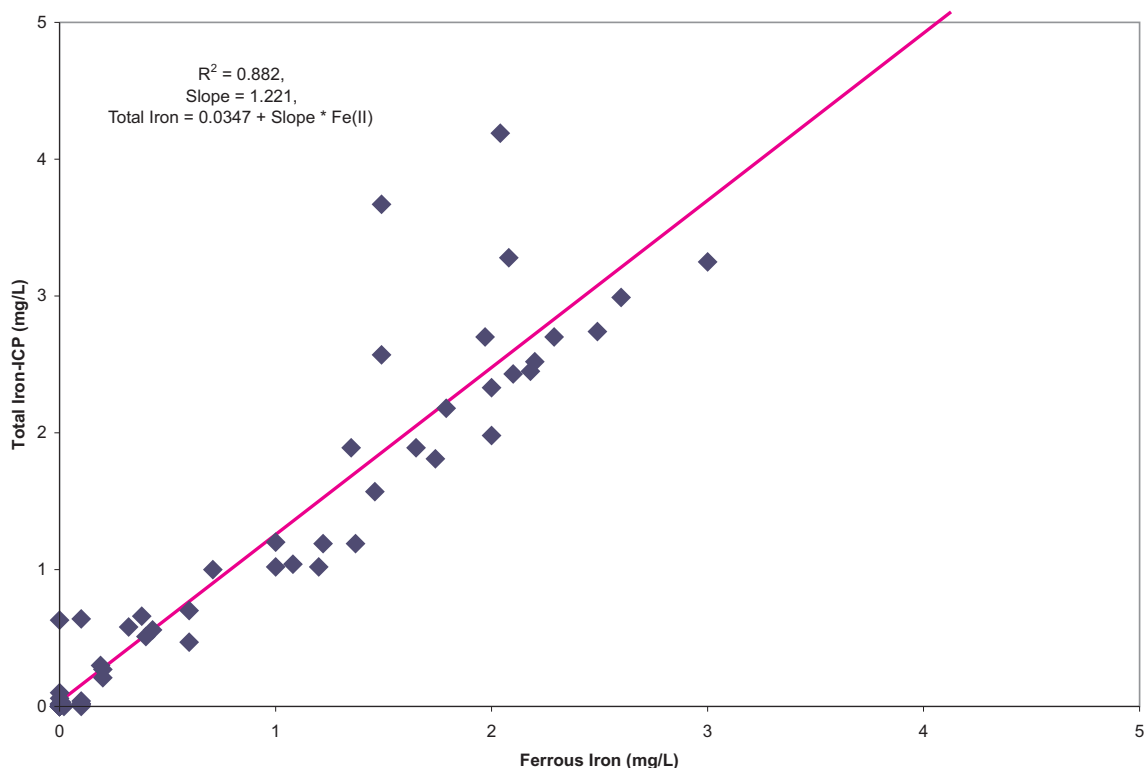
Comparisons were made between the field  $\text{Fe(II)}$  values and total Fe values determined by ICP-OES in the laboratory. Figure 5.5 shows a fairly good correlation between  $\text{Fe(II)}$  and total Fe values for ML21 which is upgradient of the barrier at the USCG site with a regression  $R^2$  of 0.89 and a slope of 1.24. Figure 5.6 shows the downgradient total iron data in ML25 to be somewhat higher than  $\text{Fe(II)}$ . This may be due to colloids passing through the filter and followed by  $\text{Fe(OH)}_3$  dissolution after acidification with  $\text{HNO}_3$ . It is important to acidify samples to  $\text{pH} < 2$  immediately after collection to prevent oxidation of  $\text{Fe(II)}$  to  $\text{Fe(III)}$  and subsequent precipitation. This would result in artificially low total Fe values compared to dissolved  $\text{Fe(II)}$  measure in the field.

### 5.1.3 Alkalinity

A Hach® digital titration kit (Method 8203) was used to determine alkalinity concentrations as  $\text{CaCO}_3$ . A 100 mL unfiltered ground-water sample was placed in a 250 mL Erlenmeyer flask and the contents of one bromocresol green-methyl red indicator packet was added. The sample was titrated using 1.6 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) until a purple/pink colorimetric endpoint ( $\text{pH} 4.5$ ) was reached. There are very few interferences with this method; however, highly turbid or colored samples may mask a true visual endpoint. If this occurs, sample  $\text{pH}$  would need to be monitored to determine when the endpoint was reached. The presence of chlorine may interfere with the indicator and impact alkalinity measurements. However, the addition of one drop of 0.1 N sodium thiosulfate will eliminate this interference.



**Figure 5.5** Analysis of ML21 comparing total iron and ferrous iron at the Elizabeth City site.



**Figure 5.6** Analysis of ML25 comparing total iron and ferrous iron at the Elizabeth City site.

### 5.1.4 Dissolved Oxygen

Dissolved oxygen (DO) was measured using CHEMets® colorimetric test kits. Rhodazine D method (White et al., 1990) was used for the 0-100 ppb or 0-1 ppm range and the indigo carmine method was used for the 1-12 ppm range. Water was allowed to flow through an overflow cell for at least three minutes, then the tip of the appropriate CHEMets® ampoule was placed in the bottom of the overflow cell, snapped off, and allowed to fill with the ground-water sample. The ampoules were visually compared with standards of known DO concentrations after allowing for the appropriate equilibration times (30 seconds for the rhodazine D method and two minutes for the indigo carmine method). It is important to note that the CHEMets® ampoules must be stored in the dark in order to prevent deterioration of the reagent.

The most difficult problem with field measurements for DO is the introduction of oxygen to the ground-water sample prior to measuring (Rose and Long, 1988). When using the overflow cell, the sample stream must be completely leak free. Copper tubing, long sections of neoprene, or other polymeric tubing should not be used with the CHEMets® test kit. Several other factors may lead to erroneously high DO values. Although using a membrane electrode is the easiest and fastest method for determining DO in the field, electrodes lack accuracy at low levels (<1 ppm) (Wilkin et al., 2001). Colorimetric tests will accurately measure DO concentrations <1 ppm, but interferences can adversely impact measurements. Since colorimetric reagents involve oxidation-reduction reactions, redox species may greatly influence results. The presence of reduced species such as Fe(III), Cr(VI), and Cu(II) can lead to inaccurate measurements when using the rhodazine D method. The presence of Fe(II), Fe(III), and nitrite has been shown to result in false measurements when using the indigo carmine method (Gilbert et al., 1982). Hydrogen sulfide apparently does not interfere with either colorimetric method, and the effects from the presence of total organic carbon (TOC) are not well understood. However, these problems can be minimized by using proper sampling techniques (Hitchman, 1978).

### 5.1.5 Hydrogen Sulfide

Hydrogen sulfide ( $H_2S$ ) was analyzed at the DFC site only. The first 25 mL of sample was collected for  $H_2S$  analysis. This analysis was conducted using the Hach® DR/2010 portable spectrophotometer using methylene blue colorimetric indicator (American Public Health Association et al., 1992). Additionally, CHEMets® sulfide ampoules (0-1 ppm range), which also utilize the methylene blue colorimetric method, were used to measure  $H_2S$  in the field. Ground water was

allowed to flow through an overflow cell for two to three minutes. The tip of the ampoule was placed in the bottom of the overflow cell, snapped off, and allowed to fill with ground water. The ampoule was allowed to equilibrate for five minutes prior to visual comparison with standards of known  $\text{H}_2\text{S}$  concentrations. This measurement was carried out rapidly to ensure that no  $\text{H}_2\text{S}$  would be lost due to degassing or oxidation. In acidic waters, sulfide reacts with N,N-dimethyl-p-phenylenediamine and ferric chloride to produce methylene blue. The resultant color is directly proportional to the sulfide concentration in the sample. The presence of strong reducing substances including sulfite, thiosulfate, and hydrosulfite may interfere with the precision of the instrument. These interfere by reducing the blue color or preventing color development. High concentrations of sulfide may also inhibit full color development. Sample dilution may be required to reduce these effects. The detection limit for the Hach DR/2010 for  $\text{S}^{2-}$  is 0.01 mg/L.

## 5.2 Laboratory Methods - Ground Water

Data quality was assessed using blanks and duplicate samples. The majority of the analytical results for blank samples were reported as not detected (ND) or below level of quantitation (BLQ), indicating little or no contaminant effects in nearly all cases. A few false positive results were seen for Cr and TCE at the USGS site. Cr values in the majority of field blanks were BLQ with all field and trip blanks at  $<0.006 \mu\text{g/L}$ . TCE contamination was only observed in June 1997 in one field blank at  $1.1 \mu\text{g/L}$  where the limit of quantitation was  $1 \mu\text{g/L}$ .

Analytical results for duplicate samples are shown in Appendices D, E, and F. Statistical analyses were performed on selected components of interest. Generally the variability of the results is low and within acceptable limits ( $<5\%$  difference). The relative percent difference (RPD) calculation shows a spread between  $0\% - 10\%$ , with some exceptions.

All ground-water samples collected from both sites were analyzed by ManTech Environmental Research Services Corporation, Ada, OK, using methods developed for, or recommended by, the U.S. EPA NRMRL. All analytical results and quality control (QC) measurements, including duplicates, known standards, spikes, and blanks, were reported to NRMRL researchers. Data for laboratory analyses for both field sites are found in Appendices A, B, and C.

### 5.2.1 Organic Analyses

VOA vials were analyzed for TCE, *cis*-DCE, 1,1-DCE, 1,1,1-TCA, and vinyl chloride by purge and trap method with a Tekmar LSC 2000 sample concentrator and Hewlett-Packard model 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID). Dissolved gases including ethene, ethane, and methane were analyzed using a Microsensor Technology Inc. (MTI) GC equipped with a thermal conductivity detector (Kampbell and Vandegrift, 1998). Quantitation limits for organics analysis were  $1 \mu\text{g/L}$ .

### 5.2.2 Cation Analyses

Cation samples were analyzed with a Perkin Elmer® Optima 3300 DV inductively coupled plasma spectrometer (ICP-OES). Concentrations of silver (Ag), aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), strontium (Sr), titanium (Ti), thallium (Tl), vanadium (V), and zinc (Zn) were determined. The analytical method involves the samples being nebulized into a spray chamber where argon carries the sample aerosol into the plasma at high temperature ( $\sim 6000 \text{ K}$ ). Sample particles become atomized, ionized, and excited. The optical emission of each element is then detected by a charge coupled device (CCD) detector. Elemental concentration is determined by comparing the resultant signal with standards of known concentration. Table 5.1 shows the instrument minimum limits of detection for each element measured.

Cation analysis using this method is ideally performed on aqueous solutions ranging from acidic to nearly neutral that are free of particles and organic substances. Total dissolved metals must be  $< 0.5\%$  dissolved matter; however,  $< 0.2\%$  is preferable.

### 5.2.3 Anion Analyses

Analyses were performed for chloride ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) using capillary electrophoresis (Waters® Quanta 4000E) method N-601 with Lachat® flow injection analyses and Mettler® DL21 autotitration. Nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) values were determined using hydrazine reduction with flow injection analysis colorimetry (Lachat Instruments® QuikChem Method 10-107-04-2-A) (Kamphake et al., 1967). Nitrate is reduced to nitrite with hydrazine sulfate. Nitrite concentration is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride. The resulting water soluble dye produces a magenta color. Nitrite alone can be determined by substituting deionized water for the hydrazine reagent. Method interferences include sulfide ion concentrations of  $10 \text{ mg/L}$ , which will cause a negative  $10\%$  error in nitrate and nitrite determinations within the range of the method ( $0.02 - 22.6 \text{ mg N/L as NO}_3^-$ ).

**Table 5.1** Detection Limits (D.L.) for Cation Analyses

Element	Min. D.L. mg/L	Element	Min. D.L. mg/L	Element	Min. D.L. mg/L
Na	0.03	K	0.8	Be	0.0005
Mg	0.07	Ca	0.01	Sr	0.0002
Ba	0.002	Ti	0.01	V	0.008
Cr	0.005	Mn	0.003	Fe	0.006
Co	0.006	Ni	0.01	Cu	0.002
Zn	0.001	Mo	0.004	Ag	0.1
Cd	0.002	Hg	0.07	B	0.1
Al	0.02	Tl	0.02	Pb	0.01
As	0.02	Sb	0.02	Se	0.02

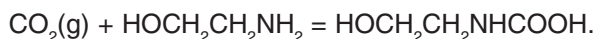
### 5.2.4 Carbon Analyses

Samples were not analyzed for total carbon (TC) and total organic carbon (TOC) concentrations for each sampling event. However, when samples were analyzed for these constituents, TC concentrations were determined using a Dohrmann® DC-80 instrument. TOC was determined by acidifying an aliquot of the sample with ultra-pure phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), purging with ultra high purity nitrogen for three minutes to remove the inorganic carbon prior to analysis. The sample was injected into a reaction chamber where organic carbon was converted to CO<sub>2</sub> followed by infrared detection.

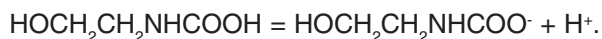
## 5.3 Laboratory Methods - Soils

### 5.3.1 Inorganic Carbon Analysis

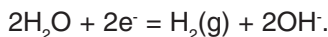
Concentrations of inorganic carbon in core samples were determined with a carbon coulometer system (UIC, Inc. Model CM5014). The carbon coulometer system measures carbon as carbon dioxide in a carrier gas (Figure 5.7). A gas stream containing carbon dioxide is evolved from a sample by acidification and then bubbled into the coulometer titration cell, which contains a CO<sub>2</sub>-sensitive ethanolamine solution and a platinum electrode (Huffman, 1977; Engleman et al., 1985). Before entering the titration cell, the gas stream is passed through a silver nitrate solution to remove potentially interfering species (e.g., hydrogen sulfide). In the titration cell, carbon dioxide reacts to form a titratable acid and causes the ethanolamine solution colorimetric pH indicator to fade from blue to clear. The incoming CO<sub>2</sub> reacts with the ethanolamine to form N-carboxy-2-amino ethanol:



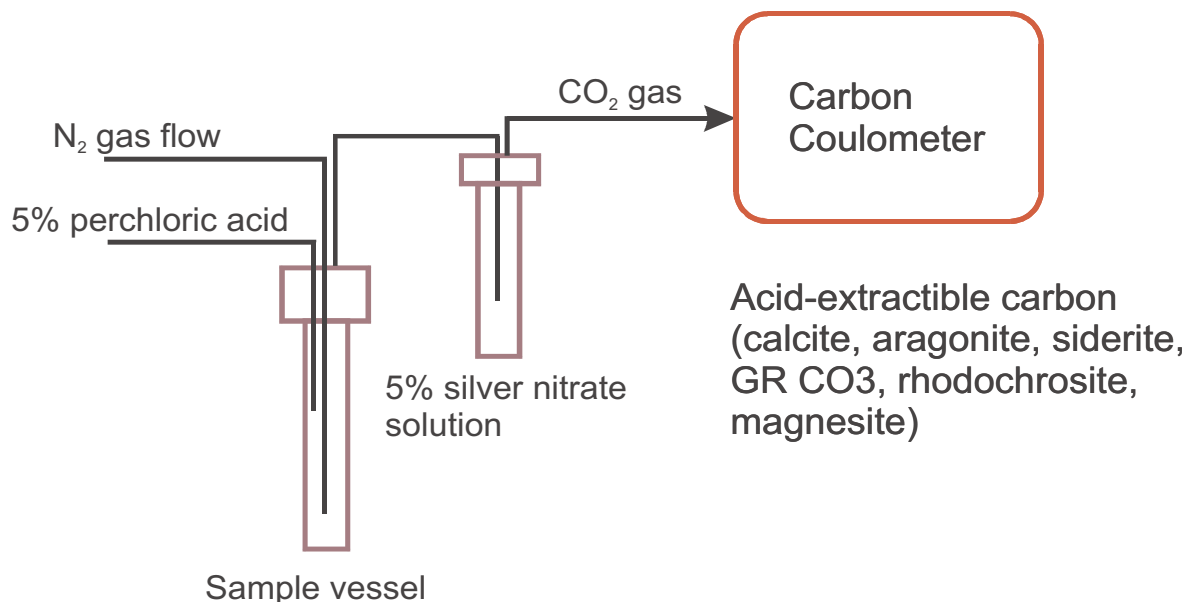
The N-carboxy-2-amino ethanol dissociates, and the pH of the solution decreases, which causes the indicator color to fade:



A photometer in the CM5014 detects the color change and initiates a current within the cell. The reaction at the platinum electrode produces OH<sup>-</sup>:



The current electrochemically generates a base at a maximum rate equivalent to about 1500 micrograms of carbon per minute. As base is produced, the pH of the cell solution gradually returns to its initial level, and the colorimetric indicator returns to blue. The amount of current necessary to reach the endpoint is electronically integrated and converted into a quantity of carbon present in the sample.



**Figure 5.7** Schematic diagram of the carbon coulometer system for core sample characterization.

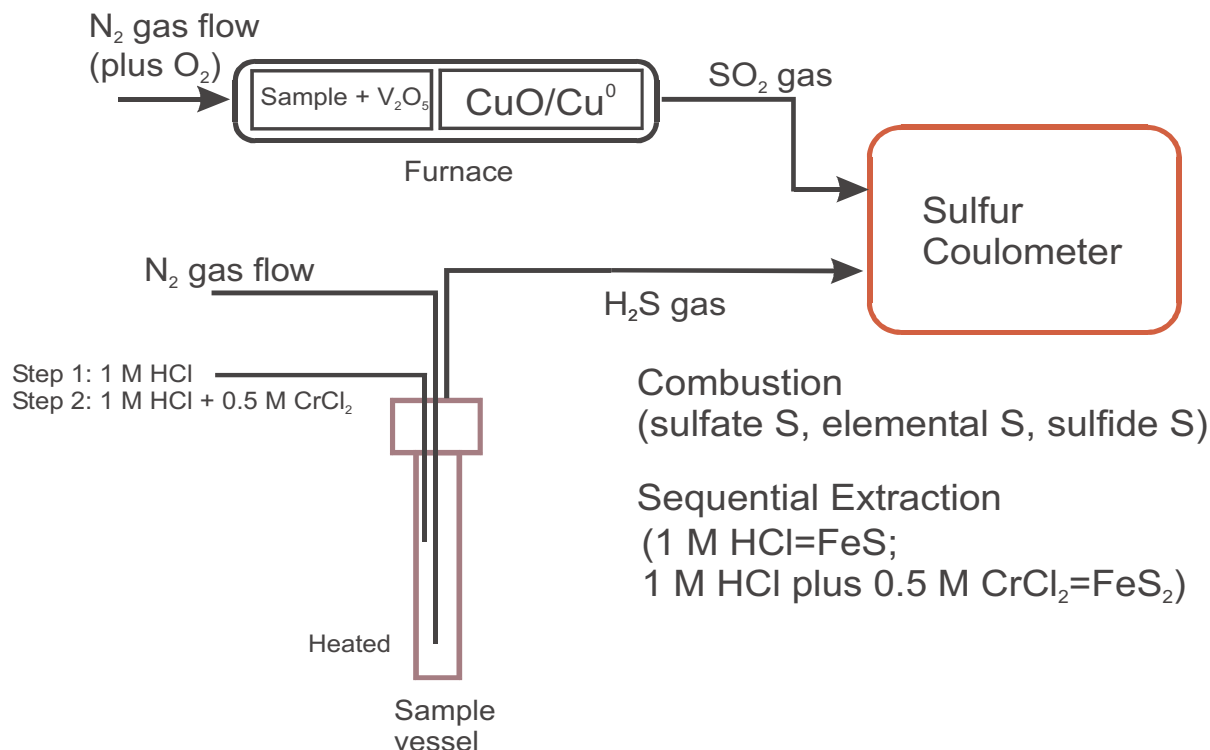
Inorganic carbon analysis results are given in weight percent C based upon carbon that is released from a sample after acidification with hot 5% phosphoric acid. This acid digestion procedure releases inorganic carbon present in minerals such as calcite (trigonal  $\text{CaCO}_3$ ), aragonite (orthorhombic  $\text{CaCO}_3$ ), siderite ( $\text{FeCO}_3$ ), magnesite ( $\text{MgCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ), iron carbonate hydroxide ( $\text{Fe}_2(\text{OH})_2\text{CO}_3$ ), and carbonate green rust ( $\text{Fe}_6(\text{OH})_{12}\text{CO}_3 \cdot n\text{H}_2\text{O}$ ). The sample size used was varied so that 0.1 to 5 mg of C was titrated. In general, sample weights of 0.5 to 5 grams were used. A typical sample analysis required 7 to 10 minutes to completely titrate all  $\text{CO}_2$  released during acidification. The detection limit was determined to be 0.001 wt % for a 1-gram sample size. Calcium carbonate (Aldrich, 99.999%) was used as a standard reference material. In all cases analysis of the reference material resulted in values within 5% of the accepted value for  $\text{CaCO}_3$  (12.0 wt% C). Results of the inorganic carbon measurements are presented and discussed in Volume 1 of this EPA Report series.

### 5.3.2 Sulfur Analysis

Measurements of total sulfur and sulfur partitioning in the solid phase was carried out using a sulfur coulometer (UIC, Inc.) that measures sulfur as  $\text{SO}_2$  or  $\text{H}_2\text{S}$  gas (Figure 5.8). A gas stream, evolved from a sample by chemical extraction or combustion, is bubbled into a coulometer titration cell, which contains an excess of iodide ( $\text{I}^-$ ) and a small concentration of free iodine ( $\text{I}_2$ ). The sulfur gases are oxidized by the iodine as they are swept through the coulometer cell. An amperometric-sensing circuit detects the loss of  $\text{I}_2$  in solution and causes more iodine to be electrochemically generated at a rate proportional to the sensed loss of concentration (maximum titration rate is 2000 micrograms S per minute). After all of the  $\text{SO}_2$  or  $\text{H}_2\text{S}$  has been titrated, the iodine is restored to its initial concentration. The total current used to generate the iodine is integrated by the coulometer and digitally displayed in operator-selected units, such as micrograms of S or micrograms of  $\text{SO}_2$ .

Concentrations of total sulfur in solid samples are determined by combustion at 1050 °C. Samples are weighed into a ceramic boat, covered with vanadium pentoxide, and introduced to a combustion furnace (Atkin and Sommerfield, 1994). The combustion products are passed over an oxidation catalyst ( $\text{CuO}$ ) to ensure complete decomposition and then over





**Figure 5.8** Schematic diagram of the sulfur coulometer system for core sample characterization.

metallic copper to convert all oxides of sulfur to  $\text{SO}_2$ . The  $\text{SO}_2$  is measured coulometrically and related to the concentration of sulfur in the sample. The instrument is most effective for samples with total sulfur values that range between 5 and 2500 micrograms. For a 0.10 gram sample, this corresponds to a sulfur concentration range of 0.005 to 2.5 wt% S. Standard reference materials for total sulfur measurements were NIST 1646a (Estuarine sediment, 0.35 wt% S) and barium sulfate (Aldrich, 99.99%, 13.75 wt% S). This combustion method is not able to completely release sulfur present within iron metal. Total sulfur values in Peerless iron obtained by other methods are typically near 0.1 wt%, but with this method total sulfur values in unreacted iron samples are less than 0.03 wt%. The method described here is sensitive, for determining the concentrations of sulfur in precipitates that have formed on the iron surfaces as a consequence of long-term ground-water exposure.

Concentrations of acid-volatile sulfide and chromium-reducible sulfur are measured either sequentially or in single-step extractions (Zhabina and Volkov, 1978; Canfield et al., 1986; Morse and Cornwell, 1987). Sulfur associated with monosulfide minerals is removed by treatment of the sample with hydrochloric acid in an inert atmosphere. Metal monosulfide minerals (e.g.,  $\text{FeS}$ ) evolve hydrogen sulfide when treated with hydrochloric acid and are therefore referred to as acid-volatile sulfides (AVS). In other methods for AVS determination, the evolved  $\text{H}_2\text{S}$  is trapped as silver sulfide (or some other metal sulfide) and the amount of sulfur is determined gravimetrically. Alternatively, the evolved hydrogen sulfide can be trapped in an alkaline solution ( $\text{NaOH}$ ) and the amount of sulfide (as bisulfide,  $\text{HS}^-$ ) determined using colorimetric methods or by using an ion-selective electrode. In the method described here, evolved hydrogen sulfide is measured with the sulfur coulometer. The advantage of this instrument is that the extraction endpoint is clearly known based on a loss of current detected in the coulometer titration cell.

The chromium-reducible sulfur (CRS) extraction targets elemental sulfur and iron disulfide (pyrite, marcasite) when used in a sequential extraction, i.e., following an AVS extraction (e.g., Canfield et al., 1986). When used in a single-step extraction, hot CRS liberates all reduced sulfur (acid-volatile sulfide + elemental sulfur + pyrite). Like the AVS extraction, the CRS extraction liberates  $\text{H}_2\text{S}$  from a sample, which is carried to the coulometer cell using an inert gas. The extracting solution is prepared by first dissolving into 0.5 N HCl a quantity of chromic chloride hexahydrate needed to bring a volume of solution to 1 N  $\text{CrCl}_3$ . Next the dark-green  $\text{Cr(III)}$  solution is drawn through a column packed with granulated Zn (a Jones Reductor). Prior to packing the column, the Zn must be amalgamated in acidic 2% mercuric chloride

solution. As the acidic Cr(III) solution is passed through the Jones Reductor, it is reduced to the chromous oxidation state, Cr(II). A pronounced color change accompanies the change in oxidation state, and the solution turns from green to blue. The Cr(II) solution is unstable and will oxidize in air, so precautions must be taken to minimize air oxidation. Fresh chromous chloride solutions are preferable for CRS determinations; however, if appropriate storage methods are used (glass-stoppered bottles, no head space), acidic Cr(II) solutions can be stored for several months with negligible loss of reactivity.

Results of the total sulfur measurements and sulfur partitioning measurements are presented and discussed in Volume 1 of this EPA Report Series.

### **5.3.3 X-ray Diffraction Analysis**

Powder X-ray diffraction analysis of core samples collected from the Elizabeth City and Denver Federal Center sites in 2000 and 2001 was conducted to determine the mineralogy of precipitates formed in the iron treatment zones. Materials for analysis were prepared by sonicating iron core samples in acetone for 10 minutes followed by filtration of the released particulates through 47 mm diameter, 0.2-micron filter paper (polycarbonate). The separated particles were mounted on a zero-background quartz plate and scanned with Cu K radiation from 3° to 80° 2-theta using a Rigaku Miniflex Diffractometer (0.5° 2 per minute). Results of the X-ray diffraction studies are presented and discussed in Volume 1 of this EPA Report series.

### **5.3.4 Electron Microscopy**

Scanning electron microscopy (SEM) was used to evaluate the morphology and spatial relationships among mineral precipitates on the surfaces of zero-valent iron particles collected at the Elizabeth City and Denver Federal Center sites. In addition, energy dispersive X-ray spectroscopy (EDS) was conducted on polished samples to determine the composition of surface precipitates on a semi-quantitative basis. Samples for SEM and EDS analysis were stored in an anaerobic glove box and then embedded in an epoxy resin. The sample mounts (1" diameter round mounts) were ground and polished using diamond abrasives and coated with a thin layer of carbon prior to being placed within the SEM sample chamber.

Secondary electron and back-scattered electron images were obtained using a JEOL 5300 SEM. The instrument was operated using a 15 to 20 kV accelerating potential and a beam current of about 10 nA. Micrographs were obtained at a range of magnifications from 50x to 5000x. Copper grids obtained from SPI Supplies (West Chester, PA) were used to verify quantitative length scales. EDS spectra were acquired using an Oxford Instruments Model 6587 EDS Unit. Elemental concentrations were calculated using INCA software and cobalt metal as a standard reference material to insure semi-quantitative accuracy. Results of the SEM/EDS studies are presented and discussed in Volume 1 of this EPA Report series.

### **5.3.5 Microbial Characterization**

Sample splits for microbial characterization by phospholipid fatty acid (PLFA) analysis were shipped frozen to Microbial Insights (Rockford, TN) where all analyses were carried out. A total of 198 samples from the Elizabeth City and Denver Federal Center sites were examined by Microbial Insights. Lipids were extracted using buffered chloroform-methanol solvents. Analysis of PLFA was carried using gas chromatography/mass spectrometry (GC/MS). Results of the PLFA measurements are presented and discussed in Volume 1 of this EPA Report series.

## **5.4 Quality Assurance/Quality Control Measures**

For each type of field analysis (i.e., alkalinity, Cr(VI), Fe<sup>2+</sup>, H<sub>2</sub>S), standards of known concentration were analyzed during each sampling event to ensure instrument accuracy and performance. For laboratory analyses, quality control (QC) measures were performed along with the sample analyses. QC included analysis of blanks, duplicates (both field and laboratory), second source standards, and check standards. The relative percent difference (RPD) was calculated for selected organic and cation data for field duplicates. These RPDs are included in Appendices D, E, and F. Relative percent difference was calculated using the following equation:

$$RPD = \frac{|x_1 - x_2|}{[(x_1 + x_2)/2]} \times 100$$

where  $X_1$  is the value of the field sample and  $X_2$  is the value of the duplicate field sample.

Table D shows data for duplicate field samples obtained from the monitoring wells at the Elizabeth City site. Values are generally <10% different for sulfate, chloride, nitrate, and nitrite. Organics, dissolved gases, and cation duplicates also

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showed fairly good agreement. Where greater differences were seen, concentrations were fairly low. Total carbon showed the greatest difference between duplicate samples.

Duplicate data from the monitoring wells from the Denver Federal Center (Table E) show all values (except one pair) for sulfate, chloride, nitrate/nitrite to be <5%. Organics duplicates were very comparable except for July 2001 which showed a 58.8% difference. Duplicates for cations showed good correlation except for iron in July 2000; however, concentrations were very low.

Table F gives duplicate field sample data for Transect 2 multi-level samplers at the Elizabeth City site. Sulfate and chloride differences were <10%. The only significant difference in nitrate/nitrite data was found in June 2000; however, concentrations were <1 mg/L.

Some differences were seen between duplicates for TOC values, notably September 1998 where concentrations were 13.2 and 2.20 mg/L, resulting in a 143% difference. Where large RPDs are seen for the organics and dissolved gases, concentrations are very low. Concentrations of most cation duplicates were very comparable except where concentrations were extremely low.

